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THE EFFECT OF MINERAL ACIDITY ON THE WEATHERING OF A PODZOLIC B-HORIZON FROM THE PRECAMBRIAN SHIELD ONTARIO, CANADA

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ABSTRACT

Podzolic B horizons from a soil on the Precambrian Shield, Ontario, Canada were collected, placed in columns and treated with distilled water, cation amended water, acidified water or cation and acid amended water over a four month period. While the cation treatment had little effect relative to the control, the acid treatment removed large quantities of Al, Si and base cations. The source of the leached Al was primarily Citrate-Dithionite-Bicarbonate extractable Al, probably some form of gibbsite. However, even more pronounced was a major within column migration of oxalate extractable Al-Si, perhaps allophane or imogolite, down the acidified columns. The weathering of primary minerals contributed little to the leaching of Al from the acidified columns. In contrast to many other acidified podzols, organically bound aluminum is not the major soil fraction contributing Al to acidic leachate in this soil.

TABLE OF CONTENTS

Abstract i

Table of Contents ii

List of Tables iii

List of Figures iv

Introduction 1

  Sample Sites and Collection 3

  Laboratory Methods 4

  Analytical Methods 6

Results 8

  Leachate Chemistry 8

  Bulk Soil Chemistry 11

  Column Al and Si Budgets 13

Discussion 17

Summary 21

Acknowledgements 21

References 22

LIST OF TABLES

Table 1 Bulk soil chemistry.

Table 2 Total accumulate leachate mass from each soil column, averages and 90% Confidence Intervals.

Table 3 Bulk soil extractions after the treatments, layer averages (per 140 g) and totals (per 1400 g).

LIST OF FIGURES

Figure 1 Concentrations over the duration of the experiment of selected parameters from the Control (DDW treatment).

Figure 2 Concentrations over the duration of the experiment of selected parameters from the Cation treatment.

Figure 3 Concentrations over the duration of the experiment of selected parameters from the Acid treatment.

Figure 4 Concentrations over the duration of the experiment of selected parameters from the Acid+Cation treatment.

Figure 5 pAl (-log[Al]) versus pH for all leachate data. Two gibbsite solubility lines are shown: the upper line is for May et al.'s (1979) "natural" gibbsite, and the lower line is for Hem and Robertson's (1967) micro-cyrstalline gibbsite.

INTRODUCTION

The impact of anthropogenic acidity on the mineral weathering of soils should be assessed in terms of mechanisms, capacities and rates because of its potential impact on forest nutrient status and toxic inorganic aluminum release (Tomlinson 1990; Driscoll 1989). Of particular interest is the source and potential pool size of inorganic aluminum in soils and how it interacts with increased soil water acidity.

While the mineral layer of soils is usually the major source of inorganic aluminum under acidic conditions (David and Driscoll 1984; LaZerte 1989; Driscoll et al. 1989), substantial amounts of organic Al may be released from the forest floor, especially if the mineral layer is thin or non-existent (Cronan and Schofield 1979; Campbell et al. 1992). In many podzolic soils, however, this organic aluminum precipitates out in the lower mineral horizons of the soil (LaZerte 1989; Mulder et al 1989b). In other podzols, especially those with large quantities of organic matter and organic aluminum already in the mineral soil, the mineral soil releases organic aluminum (David and Driscoll 1984).

Dahlgren et al. (1989) and others (LaZerte 1989; Jeffries and Hendershot 1989; Driscoll 1989; Mulder et al. 1989b) show that the solubility of some gibbsite-like aluminum hydroxide compound usually controls inorganic aluminum levels in solution in the mineral horizons of acidified soils. However Walker et al. (1988) has demonstrated the potential importance of cation exchange equilibrium and Mulder et al. (1989a) has demonstrated that the release of Al bound to organic matter in the mineral soil can also be important. In fact, Cronan and Schofield (1990) argue that "exchange sites serve as the short-term source for rapid release of Al, but that some form of aluminum trihydroxide serves as the longer term resupply reservoir..." whereas Mulder et al. (1989a; 1989b) argue that organically bound aluminum is the most important **source** of Al in mineral soil water but that gibbsite-like precipitation (perhaps in clay-interlayers) occurs under recent, acidified conditions thus controlling solution Al levels. As many podzolic soils are very low in exchangeable clay content and the mineral soils analyzed by Mulder et al. (1989a; 1989b) had relatively high organic matter contents (e.g., Bh horizons), it is not clear whether these studies are representative of all acidic podzolic B horizons found on the Precambrian Shield in Canada. In addition, there is the potential for allophane or imogolite dissolution in some podzols (e.g., Dahlgren et al. 1989; Farmer 1987).

This study was designed to determine which mineral fractions of a typical, well-studied podzolic Bf horizon on the Pre-Cambrian Shield are responsible for the leaching of Al, Si and base cations under acidic conditions. Acid treatments of soil columns followed by chemical extractions and budget calculations were used to determine the relative importance of primary mineral weathering versus secondary, amorphous mineral phase weathering and cation exchange. A future paper will report the results from a second series of experiments of different design that increases the number of podzols from the Precambrian Shield that are analyzed.

Sample Sites and Collection

Soil was collected at three sites in the Plastic Lake 1-08 watershed in the Muskoka-Haliburton region of Central Ontario, Canada on the Pre-Cambrian Shield. These upland soils are sandy, shallow (~0.5 m) humo-ferric and ferro-humic podzols underlain by granitic gneiss and amphibolite (Lozano 1987; Kirkwood and Nesbitt 1991; Law 1991). Soil mineralogy consists primarily of quartz, plagioclase feldspar, potassium feldspar, amphibole, vermiculite and iron oxides (Kirkwood and Nesbitt 1991; Law 1991) with a secondary amorphous Al-Si phase coating (Kirkwood and Nesbitt 1991; Nesbitt and Muir 1988).

Previously excavated soil pits (1-11, 1-12, and 3-14; Lozano 1987) were located and accumulated debris was removed. A composite sample was taken from the cleaned surface of Bf horizons (9-27cm, 7-24cm and 12-20cm respectively), dried at 30° to 35 °C, and then passed though a 500 micron sieve to remove roots and stones. Equal amounts of the three samples were uniformly mixed together and nine identical subsamples of 1400 grams were poured into 6.35 cm I.D. plexiglass tubes to a height of 38 cm. The initial soil chemistry of this composite sample is presented in Table 1.

Laboratory Methods

A rubber stopper was inserted in the bottom of each column and a vacuum pump attached through a collection vessel. A layer of polyester fibre above the stopper acted as a filter to prevent loss of soil. The nine columns were divided into control and treatments as follows:

-2 columns : distilled water,	"Control 1 and 2"
-2 columns : cation solution,	"Cation 1 and 2"
-2 columns : pH solution,	"pH 1 and 2"
-3 columns : cation and pH solution,	"Cation+pH 1, 2 and 3"

Two 1:500 stock solutions were made up: one pH (29 mL-conc. HNO_3/L) and one base cation (10.3 g-$CaCl_2$/L and 2.53 g-KNO_3/L) giving Ca concentrations of 7.4 mg/L, K concentrations of 2 mg/L and an initial pH of approximately 3.1 in the respective treatments. The cation concentrations were based on observed averages obtained from lysimeters underlying the A horizon of soils in the PC1-08 catchment. Cation treatments were applied because it was thought that they might have some impact on weathering rates (Muir and Nesbitt 1992).

The cation stock solution was used for the entire duration of the experiment. The original pH solution was used for a period of 6 days. Because of fears that de-nitrification might slow the acidification of the columns, the HNO_3 stock solution was replaced by an HCL stock solution (31 g-conc. HCl/L). After using this solution for 6 days preliminary results showed that acid leaching was still proceeding slowly. At this time, the strength of the HCl solution was increased 10 times (310 g-conc. HCl/L) resulting in a pH of 2.1 after dilution. The resultant equilibrium pH of column leachate (about 4.0, see below) is lower than the current pH (about 4.8) of lysimeter leachate from the B horizon of these soils (LaZerte 1989) but not unusual for European podzols experiencing high levels of acidic deposition (Mulder et al. 1989b).

We determined that 1400 g of soil absorbed approximately 150 mL of water after initial wetting. Each tube therefore, had 150 mL of the appropriate solution added to the soil four times daily. It took about 15 minutes for a vacuum pump to draw the solution into the soil. The solution stayed in contact with the soil for an additional 45 minutes after which it was removed with the vacuum pump which took about 30 minutes. This 60 to 90 minute contact time was based upon previous experiments (Wels 1989) demonstrating that one hour was sufficient time for equilibration of Si with distilled water applied to these soils. The soils used by Dahlgren et al. (1989) did not, however, reach Si equilibration until after 10 hours, but Al equilibrium was obtained within 1 hour. Cation exchange equilibrium is reached in less than one hour (Walker et al. 1988). With the final leaching for the day vacuum was applied for at least one hour to ensure that there was little water left in the samples and to prevent water-logging and anoxia.

The four individual samples per day were mixed in a clean nalgene container and weighed to verify the volume of water removed from each column during that day. Dilutions of some parameters (e.g., aluminum) were necessary for those columns which had the pH treatment (pH 1 and 2, Cat+pH 1, 2, and 3) once the pH had dropped. Over a short period some aliquots used for pH measurements were accidently diluted while some others were excessively diluted for the parameters to be measured. The experiment lasted four months during which approximately 41.4L of solution was drawn through each column. This is equivalent to 1308 cm of deposition or 13 years of rainfall at the typical rate for this area of 100 cm/yr. After the leaching experiment was completed, the soil columns were extruded and sectioned into ten equal parts of 140 grams each, spread out on plastic lined trays and allowed to air dry. Blended soil samples previously reserved to determine background values of the soil were analyzed in duplicate (Table 1), all soil column sections were analyzed singly.

Where appropriate, averages of control and acidified columns plus or minus their 90% confidence interval (C.I.) are presented. Pooled variance estimates were used to calculate the 90%C.I. of the difference between acidified and control columns (Mood et al. 1974).

Analytical Methods

All water and bulk soil analyses were performed as described in Janhurst (1992). All aqueous analyses were insensitive to DOC interference, including the ion chromatographic sulphate method. Aqueous aluminum species were estimated with a catechol violet/anion exchange method (LaZerte et al. 1988) and with the speciation calculations described in

LaZerte (1984). In addition to estimates of exchangeable cations using NaCl and exchangeable protons and aluminum using both NaCl and $CaCl_2$ standard operational estimates were made of "organic" Al (pyrophosphate extraction, McKeague 1967, corrected for NaCl exchangeable Al), "amorphous" Al-Si (oxalate extraction in the dark corrected for pyrophosphate Al; McKeague and Day 1966; Farmer et al. 1983) and "crystalline" and "amorphous" Al oxides (Citrate-Dithionite-Bicarbonate (CDB) extraction corrected for pyrophosphate Al; Mehra and Jackson 1960). Aluminum obtained from the oxalate extraction, when corrected for pyrophosphate Al, is considered a good estimate of allophane and/or imogolite (Farmer et al. 1983). The CDB extraction, when corrected for pyrophosphate Al, does extract some amorphous Al-Si (Farmer et al. 1983) but is apparently more selective for the Al oxides. Neither oxalate or CDB appear to significantly extract Al from hydroxy-interlayer vermiculite (Iyengar et al. 1981; McKeague and Day 1966).

Calculated solubility products were compared to micro-crystalline (Hem and Robertson 1967) and natural gibbsite (May et al. 1979), imogolite (Farmer and Fraser 1982) and synthetic halloysite (Hem et al. 1973) :

Gibbsite:

$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$ pK_{25}= -8.11 (May et al. 1979)

pK_{25} = -9.35 (Hem and Robertson 1967)

Imogolite:

$Al_2SiO_5(OH)_4 + 6H^+ = 2Al^{3+} + H_4SiO_4 + 3H_2O$ pK_{25}=-12.0 (Farmer and Fraser 1982)

Halloysite:

$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O$ pK_{25}= -11.28 (Hem et al. 1973)

RESULTS

Leachate Chemistry

The chemistry of leachate from the replicate columns was very similar, and thus replicate results are plotted together in Figures 1-4. A smooth line is drawn through the replicate points (and missing or discarded data) using the Distance Weighted Least Squares procedure and a tension of 0.0001 (Wilkinson et al. 1992). The smoothing procedure fails when sample dilution was so excessive that the analytical granularity is large. For example, Na, K, Ca and Mg were excessively diluted 50x in the middle of the pH treatments such that analytically the only possible values were 0, 1, 2 ... mg/L (Figure 3).

Table 2 presents the total mass leached from each column over the course for the experiment for most of the chemical constituents, along with the mean of the replicate columns and their 90% C.I. To calculate these values, we linearly interpolated missing or discarded data then summed the leachate concentrations times volumes. Totals are not presented for nitrate and ammonium because of the initial use of nitric acid. DIC results are not presented because excessive dilution caused numerous missing values. The H^+

totals should be treated with some caution because of the short period when samples were mistakenly diluted.

Base Cations and Si

In the cation treatments, leachate Ca and K concentrations eventually equilibrated to the input concentrations. For the other base cations and treatments, base cation leaching declined, sometimes rapidly, after initial peaks. Even the controls exhibited high initial peaks of base cation leaching. Magnesium levels appeared to increase in the second half of the pH treatments. Although silica levels initially declined, they also began to increase later in the pH treatments along with Mg. Both with and without the pH treatment, cation treatment effects on Na (10%, based on table 2) and Mg (4%) were small, and there was no significant difference with respect to Si. The pH treatments, however, leached substantially larger quantities of Ca (80%), Mg (154%), Na (39%) and Si (120%) from the columns relative to the DDW control. Potassium was an exception with no significant difference between the pH and control treatments.

pH, Al and F

The cation treatment developed a significantly lower pH than the control (4.8 vs. 5.1), as well as slightly elevated inorganic aluminum and fluoride levels. However, in the cation + pH treatment, this cation effect on Al and F was negligible compared to the pH effect. The pH treatment gradually reduced the pH of the treated columns during the period of base cation leaching. After the base cation leachate had been reduced to near zero, inorganic Al levels rapidly rose and then stabilized and the pH stabilized at close to 4. Fluoride levels followed the initial rapid rise of inorganic Al in the pH treatments, but then began to fall while inorganic Al and pH remained stable. Organic Al was never important, however, significant amounts (290-350 mg, table 2) of catechol unreactive Al (Total-Inorganic-Organic Al) was leached from the pH treatments. This fraction would be primarily polymeric and colloidal Al (LaZerte et al. 1988).

In general, inorganic Al and pH followed the solubility curve of Al tri-hydroxides (Figure 6) closer to Hem and Robertson's (1967) gibbsite than May et al.'s (1979). However, the acidified treatments were over saturated at the initital high pH's and there was a tendency for the Al levels to remain constant as pH dropped in the middle pH ranges. Unfortunately, there is less data for the middle pH range as all the pH results discarded because of dilution were in that range. Imogolite and synthetic halloysite were always over-saturated and Si appeared to have no relationship with Al concentrations.

DIC, DOC and sulphate

In all treatments, both DIC and DOC concentrations rapidly declined after initial peaks. Overall, there was a significant tendency for the cation treatments to decrease DOC leaching by about 12-14% and for the pH treatments to increase DOC leaching by about 25-26%. Similarly, sulphate leaching was decreased by the cation treatment: 31% below the control for the cation treatment, but only 10% below the pH treatment in the cation +

pH treatment. The pH treatment dramatically reduced sulphate leaching by about 74% when there was no cation treatment, and by 66% when there was.

Nitrate and Ammonium

In the cation treatments, leachate nitrate concentrations eventually equilibrated to the input concentrations, whereas nitrate rapidly dropped to about 10 μg/L in the control and, after switching from nitric to hydrochloric acids, in the pH treatment. All columns leached similar amounts of ammonium; initially they rose rapidly to about 3-5 mg/L, then declined rapidly to about 1 mg/L. From then on there was a steady decline in ammonium leached, down to about 200-300 μg/L at the end of the experiment.

Bulk Soil Chemistry

Results of the bulk soil chemical extractions from the columns, are presented in Table 3. The average results for individual layers (normalized to 140 g) from the columns and the summed total for 1400 g is presented.

Base Cations

The cation treatment approximately doubled the overall Ca saturation of the exchange sites over that of the reserved soil and maintained the K saturation at approximately the same level as the reserved soil. Most of the increase was in the topmost layer. However, in the pH + cation, pH and control treatments, all K was stripped from the exchange sites and only small amounts of Ca in the acidifed columns were found. Mg was depleted in all treatments including the DDW control but in the top layer under the acidified treatments slightly elevated levels developed relative to the reserved soil.

pH and Exchangeable Al

The proton content, as measured by both water and $CaCl_2$ extraction methods, decreased with the control and cation treatments, but increased dramatically with the pH treatments (in the acidified treatments both methods gave similar results, but in the control, cation and reserved soils, the $CaCl_2$ method gave larger estimates). Similarly, NaCl exchangeable Al decreased in the control and cation treatments but approximately doubled in the pH treatments. $CaCl_2$ exchangeable Al behaved similarly, approximately trebling in the pH treatments. In all cases, it was the upper layer of the columns that had the highest levels of exchangeable Al and protons.

Extractable Al and Si

There was much more extractable Al than exchangeable (>500x). All treatments, including controls, exhibited a reduction in total extracted Al and Si with respect to the reserved soils, and there was only small differences between the control totals and other treatment totals. However, in the top two layers of the columns, substantial differences are found between the pH treatments and controls (including the cation treatment) with an approximately 60%

reduction in oxalate extractable Al and Si, a 38% reduction in CDB extractable Al and a 20% difference in pyrophosphate extractable Al.

Column Al and Si Budgets

As the weathering of primary minerals generates base cations as well as Al and Si, we will use the difference in the leached base cations to estimate the relative increase in weathering derived Al and Si due to acidification of the columns. According to Kirkwood and Nesbitt (1991), the minerals weathering in the Plastic 1-08 catchment are primarily plagioclase (49 kg/ha/yr), quartz (24 kg/ha/yr) and K-feldspar (19 kg/ha/yr) with biotite/vermiculite and amphibole being of lesser importance (15.7 kg/ha/yr taken together). Their estimated Na/Ca molar ratio for the plagioclase was about 0.27-0.29 (An_{27}-An_{29}). In this experiment, the molar Na/Ca ratio was 25 ±3 for the control leachate and 19 ±1 for the acid leachate (corrected for changes on exchange sites), suggesting an increase in anorthite ($CaAl_2Si_2O_8$) over albite ($NaAlSi_3O_8$) leaching under acidic conditions. For the purposes of estimating Al and Si weathering from these primary minerals we assume that all the excess Ca and Na leached from the acidified relative to control columns was the result of anorthite and albite weathering, and that the K came from K-feldspar ($KAlSi_3O_8$). The excess Mg is probably derived from amphibole and biotite/vermiculite weathering. We will represent this weathering with a generalized Mg:Al:Si molar ratio of 2.5:2:6 (from Table 1 of Kirkwood and Nesbitt 1991). Based on these assumptions we calculate that an excess of 0.047 ±0.004 g of Al and 0.072 ±0.006 g of Si per column are released in the acidified relative to the control treatments during this experiment (excluding the columns with the cation treatment). No estimate can be made of quartz weathering from the base cation leachate data.

As the cation treatments had little impact on extractable Al and Si, their column results are averaged with the other columns. There was an average net loss of 1.08 ±0.14 g of "amorphous" Al (oxalate minus pyrophosphate extracts) in the top two layers but a net gain of 0.89 ±0.44 g in the lower layers giving an insignificant total net loss of 0.19 ±0.52 g "amorphous" Al per column (pH and pH+CATION treatments relative to the CONTROL and CATION columns). For "organic" Al (pyrophosphate extract corrected for exchangeable Al), there was an average net loss of 0.27 ±0.07 g in the top two layers and an insignificant net gain of 0.05 ±0.14 g in the lower layers giving an total net loss of 0.22 ±0.19 g Al per column. For "crystalline" Al (CDB minus pyrophosphate extracts), there was an average net loss in both the top and bottom of the columns (0.37 ±0.05 g and 0.34 ±0.19 g, respectively), giving a total net loss of 0.71 ±0.17 g Al per acidified column. In addition, exchangeable Al increased in the acidified columns relative to the controls by 0.10 ±0.01 g.

The total amount of extractable aluminum lost through acidification is difficult to calculate because of the potential overlap in Al species (allophane and amorphous sesquioxides) extracted by the oxalate and CDB procedures. Nonetheless, the fact that the oxalate Al in the bottom layers increases, whereas the CDB Al decreases, leads to the simplifying assumption that CDB and oxalate extractions (corrected for organic Al) are measuring different Al species: Al sesquioxides and allophane/imogolite respectively. Thus, the total extractable Al lost from an average acidified column relative to an average control column becomes 0.19+0.22+0.71+0.10 or 1.03 ±0.64 g Al per column. This average column loss of Al is not significantly different from the net Al leached from the acidifed columns (relative to that leached from the control columns) of 1.40 ±0.03 g and 1.06 ±0.05 g for total Al and inorganic Al respectively (Table 2). The estimate of net Al leaching from primary mineral weathering obtained earlier (0.047 ±0.004 g) is relatively insignificant when compared to the leaching of Al from extractable compounds. Although the net column loss is primarily due to CDB extractable Al, it cannot be overlooked that there has occured an even more pronounced displacement of oxalate extractable Al from the top to the lower layers in the columns.

As with amorphous Al, oxalate extractable Si was mostly moved down the acidified columns but not leached out, with an average net loss of 0.33 ±0.06 g in the top two layers and a gain of 0.38 ±0.24 in the lower layers relative to the control columns. This supports our earlier assumption that the oxalate extraction is primarily measuring allophane/imogolite. The total net gain of 0.05 ±0.30 g amorphous Si per acidified column is not significantly different from zero. If we take the net leachate loss of Si (0.21 g), add the net accumulation of oxalate extractable Si (0.05 g) and subtract the Si derived from weathering of primary minerals other than quartz (0.07 g), we obtain an estimate of acid enhanced quartz weathering that is also not significantly different from zero. Nonetheless, we suspect that substantial amounts of the Si in the leachate is derived from quartz, as demonstrated by Kirkwood and Nesbitt (1991), but that the impact of acidification on quartz weathering is minimal as demonstrated by Krauss and Wolery (1988). In general, because of the large errors in estimating the difference between oxalate extractable Si of acid treated and control columns, it is impossible to determine which soil fractions are responsible for the acid enhanced leaching of Si in this experiment.

In general, more Al than Si was leached and/or moved around in the acidified columns. The molar oxalate extractable Al/Si ratios are 2.0 ±0.1 and 2.5 ±0.1 for the average net loss in the top two layers and the gain in the lower layers of the acidified columns respectively. Childs et al. (1983) has reported ratios of 1.6-2.8 for the allophane-imogolite complex in New Zealand podzols. The Al/Si ratio was higher in the leachate, 2.9-3.7 depending upon whether inorganic or total Al is used, apparently because much more CDB Al was leached than Si derived from quartz. The over-saturation with respect to imogolite and halloysite in the leachate was in part caused by this excess aluminum. This probably drove the re-precipitation of amorphous Al and Si in the lower part of the columns, perhaps as allophane or imogolite (Farmer 1987). Dahlgren and Ugolini (1989) and Farmer (1987) have proposed a simultaneous equilibrium between an aluminum tri-hydroxide and imogolite such that:

$$2Al(OH)_3(s) + H_4SiO_4 = Al_2SiO_3(OH)_4(s) + 3H_2O \qquad pK_{25} = 4.1$$

This reaction provides an equilibrium Si concentration of about 2.2 mg/L which is similar to that observed in the field (LaZerte, unpublished results) but much lower than that observed in the acidic treatment columns.

DISCUSSION

The control and all treatments leached much more ammonium than found under field conditions (LaZerte, unpublished results). It is not uncommon in soil column experiments like this for large amounts of ammonium and nitrate to be generated from the breakdown of organic nitrogen in the soils (Skeffington and Brown 1986). Since all columns leached similar amounts of ammonium, including the those intially acidified with nitric acid, it is most likely that organic-N was the major source. The process can potentially alter the acidity of the columns. Also, ammonium competes with base cations for exchange sites and may be partially responsible for the depletion of exhangeable cations, especially in the controls. Although this can complicate the interpreation of base cation weathering, it has little impact on our interpretation of the Al and Si results and the weathering processes involved.

The major effect of the cation treatment was to decrease DOC and sulphate leaching 10-30%. It also lowered the pH and raised inorganic Al slightly. In general, these were not major effects and for our purposes can be ignored relative to the pH treatment. The pH treatment also affected sulphate (decrease) and DOC (increase) leaching. By increasing anion adsorption sites, the pH treatments induce the sulphate strong acid anion to be bound more tightly (Mitchell et al. 1990) and less leaching is observed in the field under acidified conditions as well. Conversely, the DOC weak acid anions are more highly protonated under acidic conditions perhaps causing less adsorption. However, field studies generally show a decrease in DOC leaching with acidification (Marmorek et al. 1987).

More importantly however, the pH treatment, relative to the control, had several very dramatic effects. The most significant, for the purposes of this study, is the rapid loss of base saturation and subsequent increase in Al and F in solution, followed by the stabilization of both pH and inorganic Al and the fall in F. Exchangeable bases initially buffered the pH decline until they were depleted and the exchange sites populated with protons and Al; then inorganic Al solids began to buffer the pH. The predicted equilibium pH for a solution of pH 2.1 brought into contact with an aluminum tri-hydroxide compound with pK_{sp} of -9.35 (Hem and Robertson 1967) is about 3.98, very close to that obtained in the pH treatments (4.0). Equilibrium pHs this low are not unusual in the B horizons of highly acidified European podzols (e.g., the sandy Dutch Tongbersven soil; Mulder et al. 1989b).

David and Driscoll (1984) and Johnson et al. (1981) have suggested that the fluoride in soil waters comes directly from weathering. Our results are not consistent with this interpretation; the onset of fluoride leaching corresponds directly with the onset of amorphous Al leaching and then declines rapidly with the peak in fluoride leaching coinciding with a plateau in Al levels. We propose that although initially fluoride must come from weathering (most likely from mica: H.W. Nesbitt, personal communication), it is usually accumulated in these soils as mixed Al-F-OH on the surface of amorphous Al compounds in the soil. Natural cycles of dissolution and re-precipitation might permit the continual migration of fluoride to the surface as mixed Al-F-OH compounds would be more soluble than pure aluminum tri-hydroxides.

The increased levels of Mg and Si in the acidified column leachate toward the latter half of the experiment coupled with the increased levels of exchangeable Mg in the upper layers of the acidifed columns suggest that the intense acidification of the top layer of the columns accelerated the dissolution of some Mg-Si mineral, perhaps vermiculite. However, it is clear from the selective extraction results and column budgets that the major component responsible for aluminum mobilization within the columns was oxalate extractable aluminum, perhaps allophane or imogolite.

We propose that, in the lower part of the acidified columns, solution Al was in equilibrium with a gibbsite-like material which was both dissolving to form aqueous Al and to buffer the pH and reacting with solution Si to form solid phase allophane or imogolite. However, solution Si was not reacting fast enough with the amorphous gibbsite for equilibrium between Si and allophane/imogolite to occur. This lack of equilibrium may be because the one hour equilibration time used in these experiments is too short when Si is in excess. The one hour equilibration was based on experiments with distilled water (Wels 1989) but Dahlgren et al. (1989) used a 10 hour equilibration time. In addition, the continual dissolution of gibbsite in the lower part of these acidified columns may have somehow impeded the reaction with Si.

Farmer (1987) argues that in natural soils a pH higher than 4.9 is needed to precipitate allophane/imogolite but his conclusions are based on correlations with field data obtained under natural conditions of soil development. The experiments presented here suggest that an oxalate extractable Al-Si can form at pH 4 with an Al/Si molar ratio approximating that of allophane/imogolite. As neither oxalate nor CDB extractions apparently extract hydroxy-interlayer aluminum, then it cannot be hydroxy-interlayer Al in vermiculite that is being removed in the top of the acidified columns and being deposited and reacting with solution Si to form allophane/proto-imogolite in the bottom.

By way of contrast to the Plastic Lake podzol analyzed here, in the Pancake Creek, New York, U.S.A. podzols studied by Driscoll et al. (1989) and the Huntington Forest, New York, U.S.A. soils studied by David and Driscoll (1984), all the oxalate extractable Al was also pyrophosphate extractable (organic). Similarly, the soil horizons studied by Mulder et al. (1989a; 1989b) were organic rich Bh horizons with high levels of pyrophosphate extractable Al. Under these conditions, it is not unreasonable for Mulder et al. (1989a; 1989b) to find that organic Al is the primary source of Al under acidic conditions. As aluminum is released from the organic phase and the solution is neutralized, aluminum tri-hydroxide precipitation could occur inducing the observed gibbsite-like solubility relationship (Mulder et al. 1989a; 1989b).

The importance that Cronan and Schofield (1990) attribute to soil exchange sites as a short-term source of solution aluminum "resupplied" by some aluminum tri-hydroxide does not appear to apply to the experiments presented here. Rather, readily exchangeable aluminum appears to be **controlled** by solution concentrations of aluminum which are, in turn, controlled by the solubility of some aluminum tri-hydroxide. In general, under equilibrium conditions, the largest pool size (solid phase aluminum trihydroxide) should control smaller pool sizes (solution and exchangeable Al).

SUMMARY

We conclude that amorphous minerals are the major source of Al leached from soils under acidic conditions. While Al-Silicates are readily mobilized, they are just as readily precipitated within the soil horizon, whereas amorphous gibbsites are leached out. The acidic weathering of primary minerals does not contribute much Al to leachates. We cannot determine from this experiment whether the increased levels of Si in acidified leachate are the result of increased weathering of primary minerals or amorphous Al-Silicates. Unlike soils with larger amounts of organic matter in their mineral horizons, most of the Al leached from these Plastic Lake soils is not organically bound.

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Table 1. Bulk Soil Chemistry

Si, Oxal.	% by wgt.	0.44
Al,Oxal.	% by wgt.	1.60
Al, CDB	% by wgt.	0.89
Al, Pyro.	% by wgt.	0.50
Al, Exch.	meq/100g	0.630
Ca, Exch.	meq/100g	0.075
K, Exch.	meq/100g	0.050
Mg, Exch.	meq/100g	0.045
CEC	meq/100g	0.800
Al, CaCl	ug/g	7.45
pH, CaCl		4.48
pH, H2O		4.92
Clay	% by wgt.	2
Silt	% by wgt.	31
Sand	% by wgt.	67
Org. C	% by wgt.	2.77

Table 2. Total accumulated leachate

	H+	Tot Al	Org Al	Inorg Al	F	Ca	Mg	K	Na	SO4	DOC	Si
	umole	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg
PC-CTRL1	508	11	1.6	4	0.7	34	5.8	35	4.4	257	159	180
PC-CTRL2	505	11	1.6	4	0.7	32	5.5	33	4.5	253	153	176
AVG.	507	11	1.6	4	0.7	33	5.7	34	4.5	255	156	178
90% C.I.	5	0	0.1	0	0.0	3	0.5	3	0.2	7	8	6
PC-CAT1	822	14	1.5	8	1.4	207	6.0	86	4.9	175	136	179
PC-CAT2	817	14	1.6	8	1.4	211	5.9	88	4.9	178	137	180
AVG.	820	14	1.6	8	1.4	209	5.9	87	4.9	177	136	179
90% C.I.	7	0	0.1	1	0.0	6	0.1	3	0.1	4	0	2
PC-PH1	6586	1383	4.2	1022	31.1	60	14.0	36	6.2	67	193	385
PC-PH2	6411	1429	3.5	1096	31.8	58	14.9	36	6.2	66	197	395
AVG.	6499	1406	3.8	1059	31.5	59	14.5	36	6.2	67	195	390
90% C.I.	270	71	1.0	114	1.1	4	1.5	1	0.1	2	6	15
PC-CAT+PH1	6457	1336	3.7	1099	31.7	262	11.2	105	8.8	60	179	383
PC-CAT+PH2	6419	1435	3.8	1105	32.0	259	11.6	105	9.0	56	162	391
PC-CAT+PH3	6288	1389	3.9	1097	31.8	254	10.2	107	8.8	61	176	391
AVG.	6388	1387	3.8	1100	31.8	258	11.0	106	8.9	59	172	388
90% C.I.	97	54	0	5	0	4	1	1	0	3	10	5

Table 3a

Si – oxalate extractable (g/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	0.490	0.490	0.175	0.205
3.81 to 7.6 cm.	0.497	0.469	0.427	0.471
7.61 to 11.4 cm.	0.497	0.455	0.497	0.546
11.41 to 15.2 cm.	0.476	0.490	0.497	0.537
15.21 to 19.0 cm.	0.490	0.469	0.560	0.551
19.01 to 22.8 cm.	0.525	0.462	0.497	0.532
22.81 to 26.6 cm.	0.483	0.497	0.525	0.518
26.61 to 30.4 cm.	0.490	0.490	0.504	0.518
30.41 to 34.2 cm.	0.490	0.434	0.504	0.546
34.21 to 38 cm.	0.483	0.448	0.511	0.555
TOTAL 1400 grams	4.921	4.704	4.697	4.979

Al – oxalate extractable (g/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	1.764	1.995	0.777	0.770
3.81 to 7.6 cm.	1.764	1.883	1.673	1.610
7.61 to 11.4 cm.	1.757	1.799	1.932	2.021
11.41 to 15.2 cm.	1.876	1.799	1.995	1.937
15.21 to 19.0 cm.	1.890	1.764	2.016	1.993
19.01 to 22.8 cm.	1.778	1.764	1.834	1.932
22.81 to 26.6 cm.	1.827	1.841	1.960	1.937
26.61 to 30.4 cm.	1.806	1.799	1.932	1.825
30.41 to 34.2 cm.	1.883	1.785	1.897	1.909
34.21 to 38 cm.	1.792	1.883	1.918	1.965
TOTAL 1400 grams	18.137	18.312	17.934	17.897

Al – dithionite extractable (g/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	1.176	1.302	0.756	0.770
3.81 to 7.6 cm.	1.162	1.190	1.092	1.036
7.61 to 11.4 cm.	1.148	1.183	1.183	1.162
11.41 to 15.2 cm.	1.127	1.204	1.134	1.143
15.21 to 19.0 cm.	1.155	1.176	1.204	1.134
19.01 to 22.8 cm.	1.176	1.134	1.141	1.167
22.81 to 26.6 cm.	1.183	1.253	1.155	1.120
26.61 to 30.4 cm.	1.169	1.197	1.204	1.097
30.41 to 34.2 cm.	1.232	1.169	1.190	1.157
34.21 to 38 cm.	1.232	1.162	1.155	1.111
TOTAL 1400 grams	11.760	11.970	11.214	10.897

Al – pyrophosphate extractable (g/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	0.658	0.728	0.539	0.518
3.81 to 7.6 cm.	0.644	0.700	0.707	0.681
7.61 to 11.4 cm.	0.658	0.749	0.638	0.653
11.41 to 15.2 cm.	0.644	0.651	0.700	0.705
15.21 to 19.0 cm.	0.686	0.686	0.693	0.705
19.01 to 22.8 cm.	0.686	0.658	0.665	0.700
22.81 to 26.6 cm.	0.707	0.672	0.658	0.663
26.61 to 30.4 cm.	0.637	0.686	0.651	0.686
30.41 to 34.2 cm.	0.665	0.672	0.637	0.663
34.21 to 38 cm.	0.700	0.665	0.700	0.709
TOTAL 1400 grams	6.685	6.867	6.608	6.683

Al – sodium chloride extractable (meq/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	0.371	0.301	4.718	4.219
3.81 to 7.6 cm.	0.581	0.399	2.646	2.492
7.61 to 11.4 cm.	0.637	0.511	1.813	1.582
11.41 to 15.2 cm.	0.623	0.588	1.372	1.246
15.21 to 19.0 cm.	0.644	0.588	1.246	1.106
19.01 to 22.8 cm.	0.637	0.560	1.232	1.059
22.81 to 26.6 cm.	0.686	0.581	1.190	1.059
26.61 to 30.4 cm.	0.658	0.532	1.134	1.045
30.41 to 34.2 cm.	0.665	0.616	1.078	1.050
34.21 to 38 cm.	0.658	0.560	1.022	1.069
TOTAL 1400 grams	6.160	5.236	17.451	15.927

Ca – sodium chloride extractable (meq/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	0.000	0.364	0.021	0.089
3.81 to 7.6 cm.	0.000	0.203	0.014	0.047
7.61 to 11.4 cm.	0.000	0.203	0.014	0.023
11.41 to 15.2 cm.	0.000	0.147	0.007	0.019
15.21 to 19.0 cm.	0.000	0.140	0.000	0.019
19.01 to 22.8 cm.	0.000	0.182	0.000	0.019
22.81 to 26.6 cm.	0.000	0.196	0.000	0.019
26.61 to 30.4 cm.	0.000	0.196	0.007	0.019
30.41 to 34.2 cm.	0.000	0.203	0.000	0.019
34.21 to 38 cm.	0.000	0.175	0.000	0.028
TOTAL 1400 grams	0.000	2.009	0.063	0.299

Table 3b

K - sodium chloride extractable (meq/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	0.000	0.084	0.000	0.005
3.81 to 7.6 cm.	0.000	0.077	0.000	0.000
7.61 to 11.4 cm.	0.000	0.070	0.000	0.000
11.41 to 15.2 cm.	0.000	0.063	0.007	0.000
15.21 to 19.0 cm.	0.000	0.056	0.000	0.000
19.01 to 22.8 cm.	0.000	0.133	0.000	0.000
22.81 to 26.6 cm.	0.007	0.042	0.000	0.000
26.61 to 30.4 cm.	0.000	0.042	0.000	0.000
30.41 to 34.2 cm.	0.000	0.056	0.000	0.000
34.21 to 38 cm.	0.007	0.042	0.000	0.000
TOTAL 1400 grams	0.014	0.665	0.007	0.005

Mg - sodium chloride extractable (meq/140

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	0.000	0.000	0.112	0.107
3.81 to 7.6 cm.	0.000	0.000	0.000	0.000
7.61 to 11.4 cm.	0.000	0.000	0.000	0.000
11.41 to 15.2 cm.	0.000	0.000	0.007	0.000
15.21 to 19.0 cm.	0.000	0.000	0.000	0.000
19.01 to 22.8 cm.	0.000	0.000	0.000	0.000
22.81 to 26.6 cm.	0.000	0.000	0.000	0.000
26.61 to 30.4 cm.	0.000	0.000	0.000	0.000
30.41 to 34.2 cm.	0.000	0.000	0.000	0.000
34.21 to 38 cm.	0.000	0.000	0.000	0.000
TOTAL 1400 grams	0.000	0.000	0.119	0.107

Cation exchange capacity (meq/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	0.371	0.749	4.851	1.097
3.81 to 7.6 cm.	0.581	0.679	2.660	4.424
7.61 to 11.4 cm.	0.637	0.784	1.827	2.539
11.41 to 15.2 cm.	0.623	0.798	1.372	1.605
15.21 to 19.0 cm.	0.644	0.784	1.246	1.265
19.01 to 22.8 cm.	0.637	0.875	1.232	1.125
22.81 to 26.6 cm.	0.693	0.805	1.190	1.078
26.61 to 30.4 cm.	0.658	0.770	1.141	1.078
30.41 to 34.2 cm.	0.665	0.875	1.078	1.064
34.21 to 38 cm.	0.665	0.777	1.022	1.069
TOTAL 1400 grams	6.174	7.896	17.619	16.343

Al - CaCl2 extractable (ug/140g)

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	392	322	7000	6393
3.81 to 7.6 cm.	483	441	4970	4573
7.61 to 11.4 cm.	469	504	3290	3173
11.41 to 15.2 cm.	560	381	2800	2380
15.21 to 19.0 cm.	539	630	2380	2380
19.01 to 22.8 cm.	539	630	2450	2333
22.81 to 26.6 cm.	539	714	2380	2473
26.61 to 30.4 cm.	560	665	2520	2333
30.41 to 34.2 cm.	574	742	2170	2287
34.21 to 38 cm.	567	665	2380	2520
TOTAL 1400 grams	5222	5894	32340	30847

pH - calcium chloride extractable

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	4.66	4.75	3.50	3.51
3.81 to 7.6 cm.	4.61	4.69	4.08	4.07
7.61 to 11.4 cm.	4.59	4.65	4.34	4.30
11.41 to 15.2 cm.	4.60	4.64	4.36	4.34
15.21 to 19.0 cm.	4.60	4.64	4.37	4.36
19.01 to 22.8 cm.	4.60	4.61	4.37	4.36
22.81 to 26.6 cm.	4.58	4.62	4.37	4.36
26.61 to 30.4 cm.	4.58	4.64	4.37	4.37
30.41 to 34.2 cm.	4.62	4.61	4.37	4.36
34.21 to 38 cm.	4.60	4.61	4.37	4.36

pH - water extractable

SECTION THICKNESS from the top	CONTROL	CATION	PH	CATION + PH
0 to 3.8 cm.	5.20	5.38	3.71	3.65
3.81 to 7.6 cm.	5.10	5.26	4.05	4.02
7.61 to 11.4 cm.	5.11	5.23	4.22	4.17
11.41 to 15.2 cm.	5.08	5.25	4.22	4.20
15.21 to 19.0 cm.	5.09	5.18	4.22	4.21
19.01 to 22.8 cm.	5.12	5.12	4.22	4.20
22.81 to 26.6 cm.	5.10	5.09	4.22	4.21
26.61 to 30.4 cm.	5.12	5.10	4.23	4.21
30.41 to 34.2 cm.	5.09	5.08	4.22	4.21
34.21 to 38 cm.	5.10	5.10	4.22	4.22

Fig. 1a

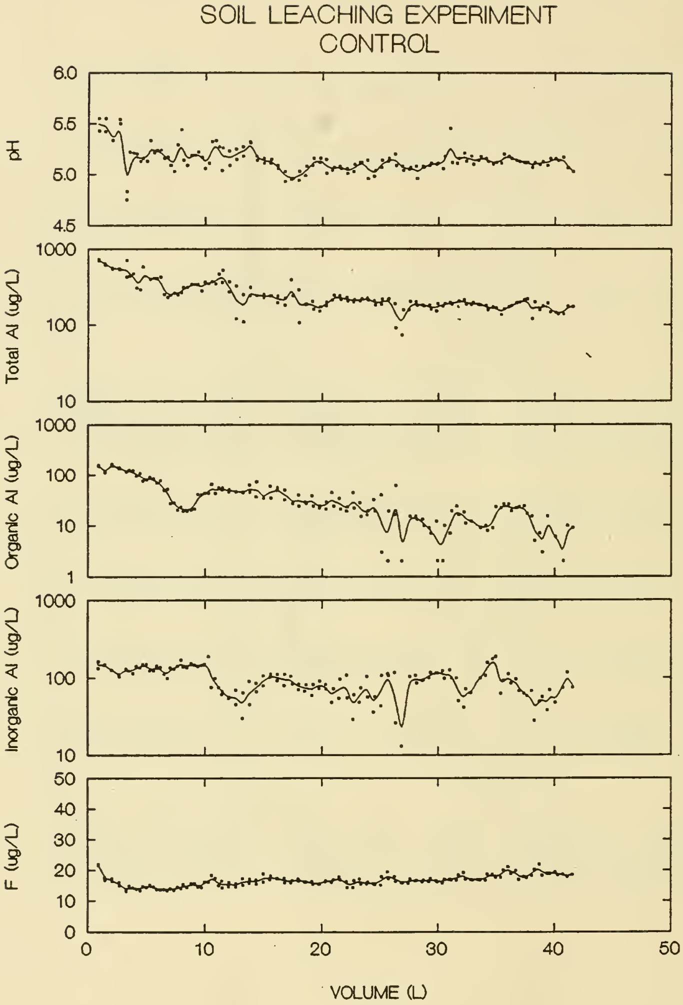

SOIL LEACHING EXPERIMENT
CONTROL
pH
6.0
5.5
5.0
4.5
Total Al (ug/L)
1000
100
10
Organic Al (ug/L)
1000
100
10
1
Inorganic Al (ug/L)
1000
100
10
F (ug/L)
50
40
30
20
10
0
0
10
20
30
40
50
VOLUME (L)

Fig. 1b

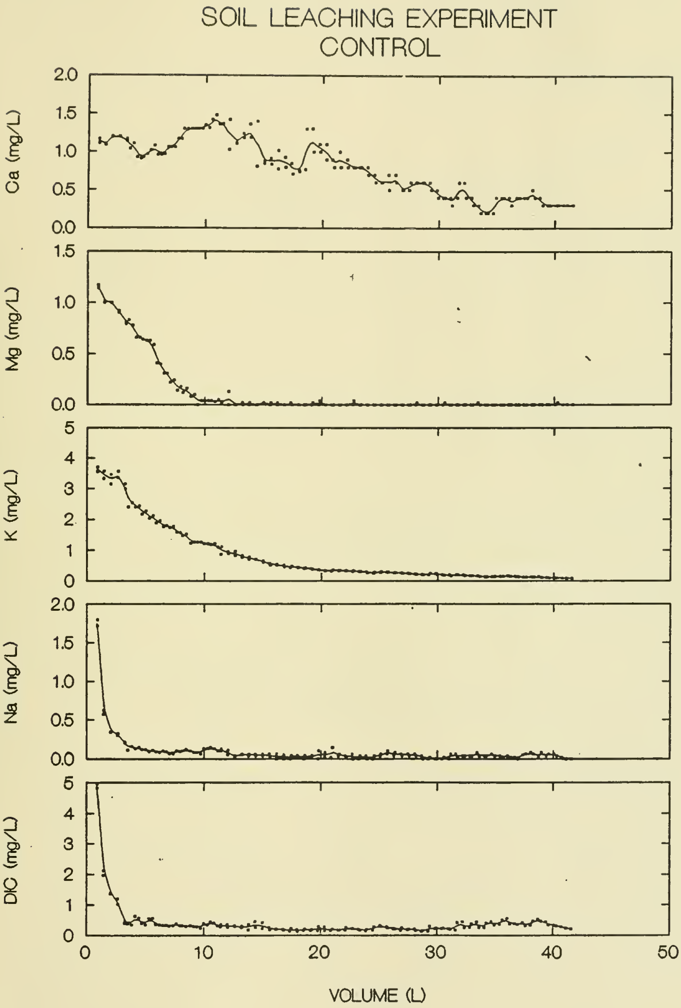

SOIL LEACHING EXPERIMENT
CONTROL
Ca (mg/L)
0.0
0.5
1.0
1.5
2.0
Mg (mg/L)
0.0
0.5
1.0
1.5
K (mg/L)
0
1
2
3
4
5
Na (mg/L)
0.0
0.5
1.0
1.5
2.0
DIC (mg/L)
0
1
2
3
4
5
0
10
20
30
40
50
VOLUME (L)

Fig. 1c

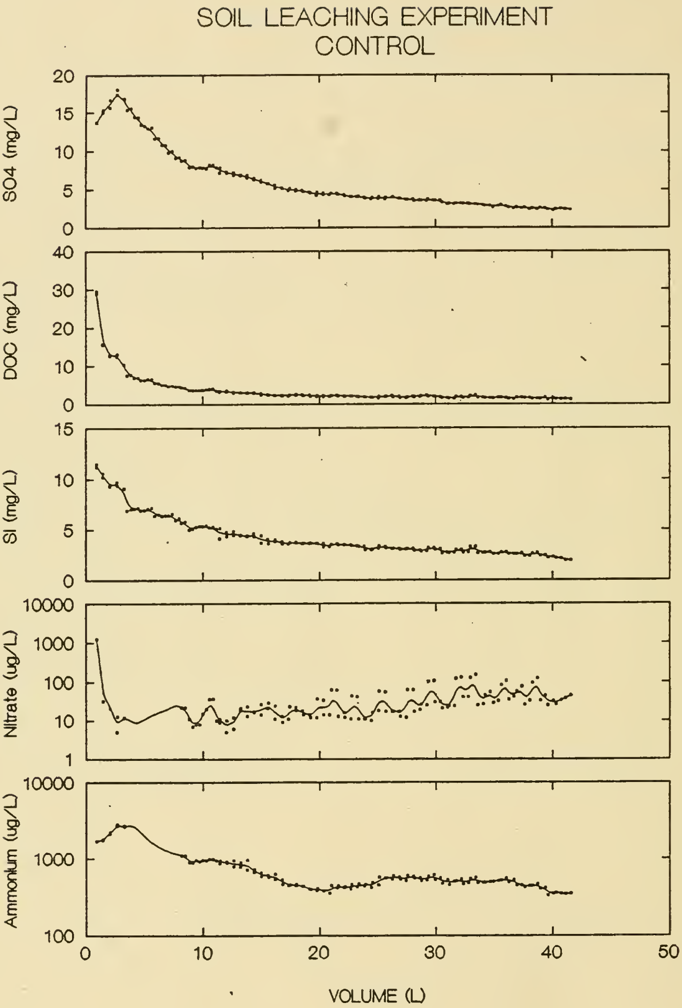

SOIL LEACHING EXPERIMENT
CONTROL
SO4 (mg/L)
20
15
10
5
0
DOC (mg/L)
40
30
20
10
0
SI (mg/L)
15
10
5
0
Nitrate (ug/L)
10000
1000
100
10
1
Ammonium (ug/L)
10000
1000
100
0
10
20
30
40
50
VOLUME (L)

Fig. 2a

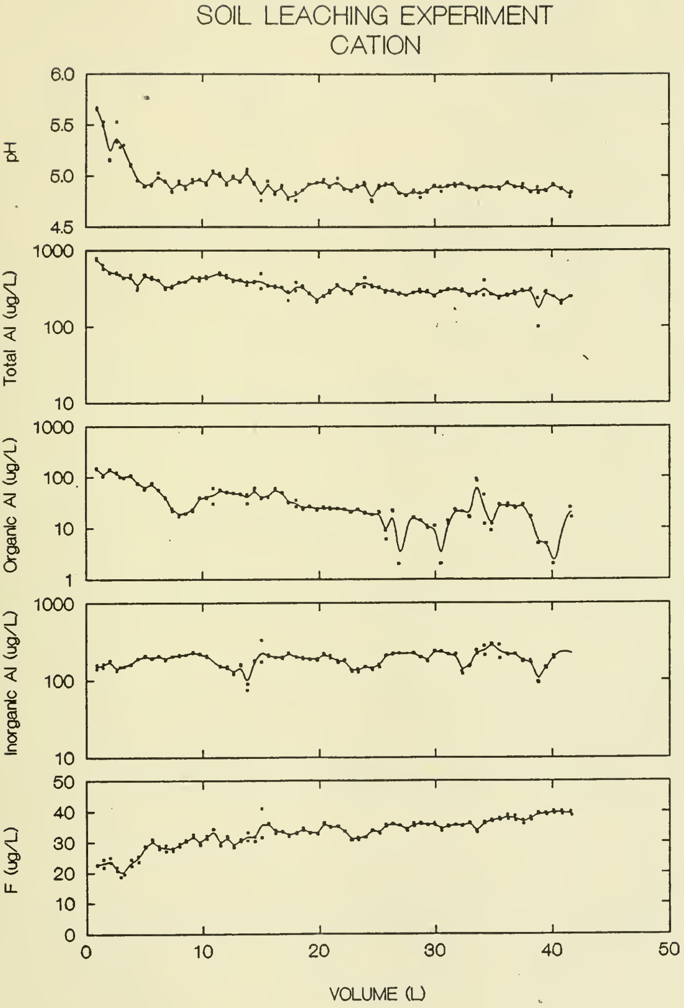

SOIL LEACHING EXPERIMENT
CATION
pH
6.0
5.5
5.0
4.5
Total Al (ug/L)
1000
100
10
Organic Al (ug/L)
1000
100
10
1
Inorganic Al (ug/L)
1000
100
10
F (ug/L)
50
40
30
20
10
0
0
10
20
30
40
50
VOLUME (L)

Fig. 2b

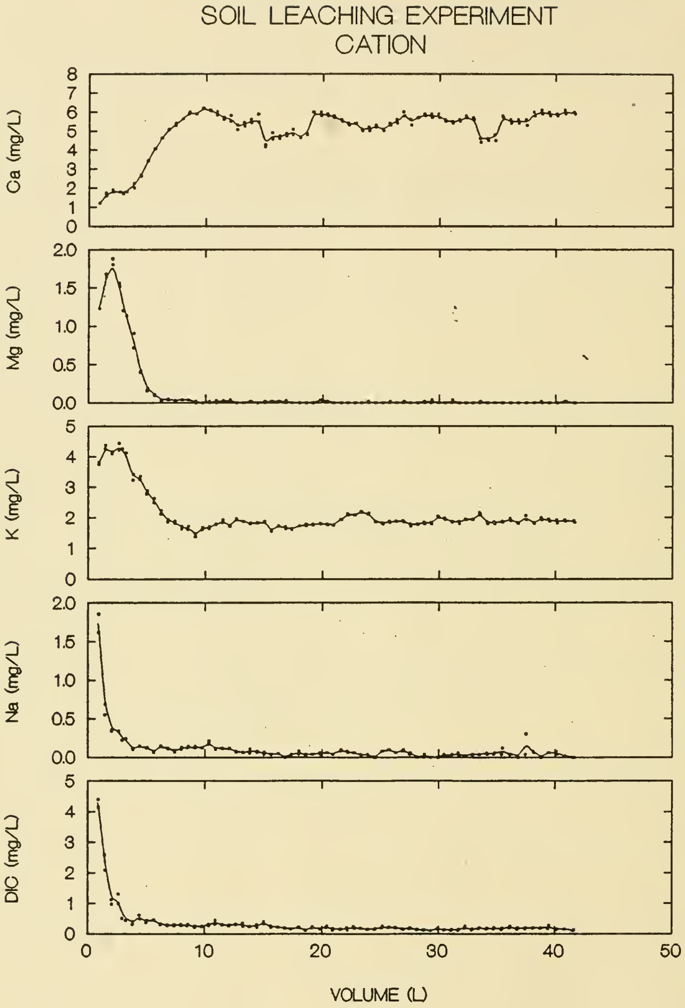

SOIL LEACHING EXPERIMENT
CATION
Ca (mg/L)
0
1
2
3
4
5
6
7
8
Mg (mg/L)
0.0
0.5
1.0
1.5
2.0
K (mg/L)
0
1
2
3
4
5
Na (mg/L)
0.0
0.5
1.0
1.5
2.0
DIC (mg/L)
0
1
2
3
4
5
0
10
20
30
40
50
VOLUME (L)

Fig. 2c

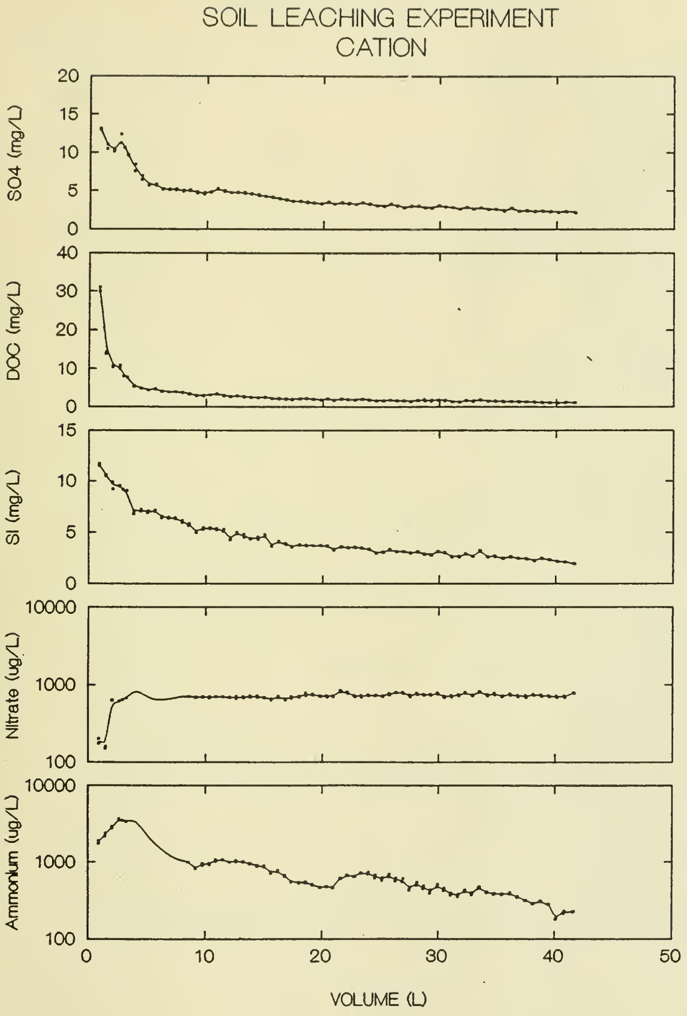

SOIL LEACHING EXPERIMENT
CATION
SO4 (mg/L)
20
15
10
5
0
DOC (mg/L)
40
30
20
10
0
SI (mg/L)
15
10
5
0
Nitrate (ug/L)
10000
1000
100
Ammonium (ug/L)
10000
1000
100
0
10
20
30
40
50
VOLUME (L)

Fig. 3a

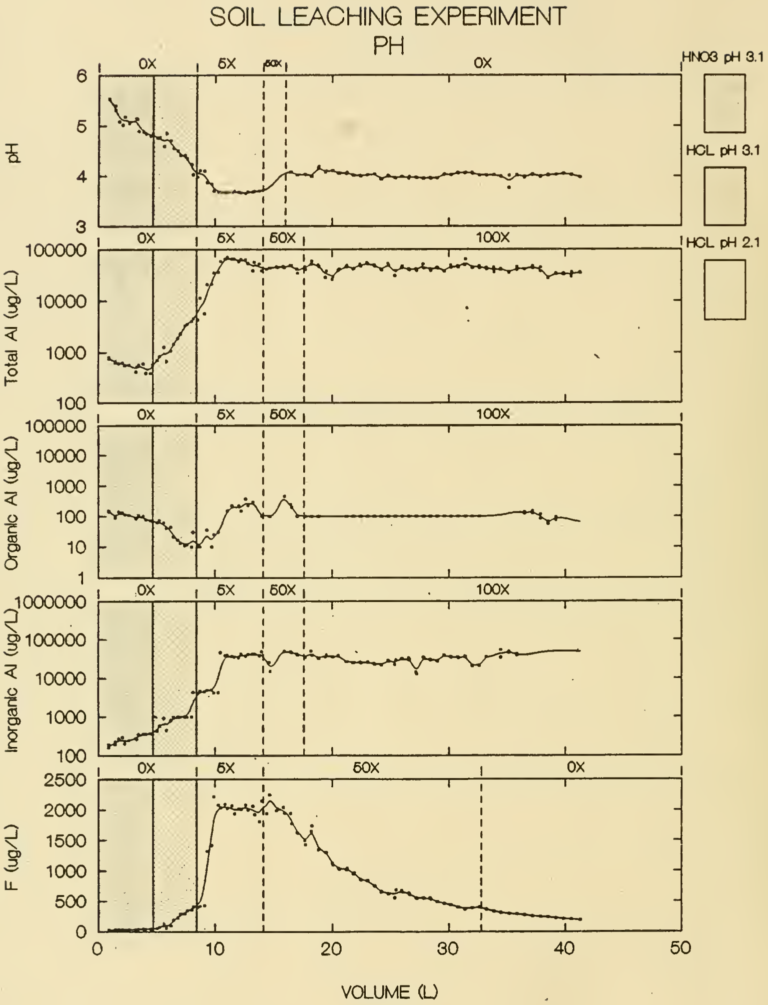

SOIL LEACHING EXPERIMENT
PH
0X
5X
50X
0X
HNO3 pH 3.1
HCL pH 3.1
HCL pH 2.1
pH
6
5
4
3
0X
5X
50X
100X
Total Al (ug/L)
100000
10000
1000
100
0X
5X
50X
100X
Organic Al (ug/L)
100000
10000
1000
100
10
1
0X
5X
50X
100X
Inorganic Al (ug/L)
1000000
100000
10000
1000
100
0X
5X
50X
0X
F (ug/L)
2500
2000
1500
1000
500
0
0
10
20
30
40
50
VOLUME (L)

Fig. 3b

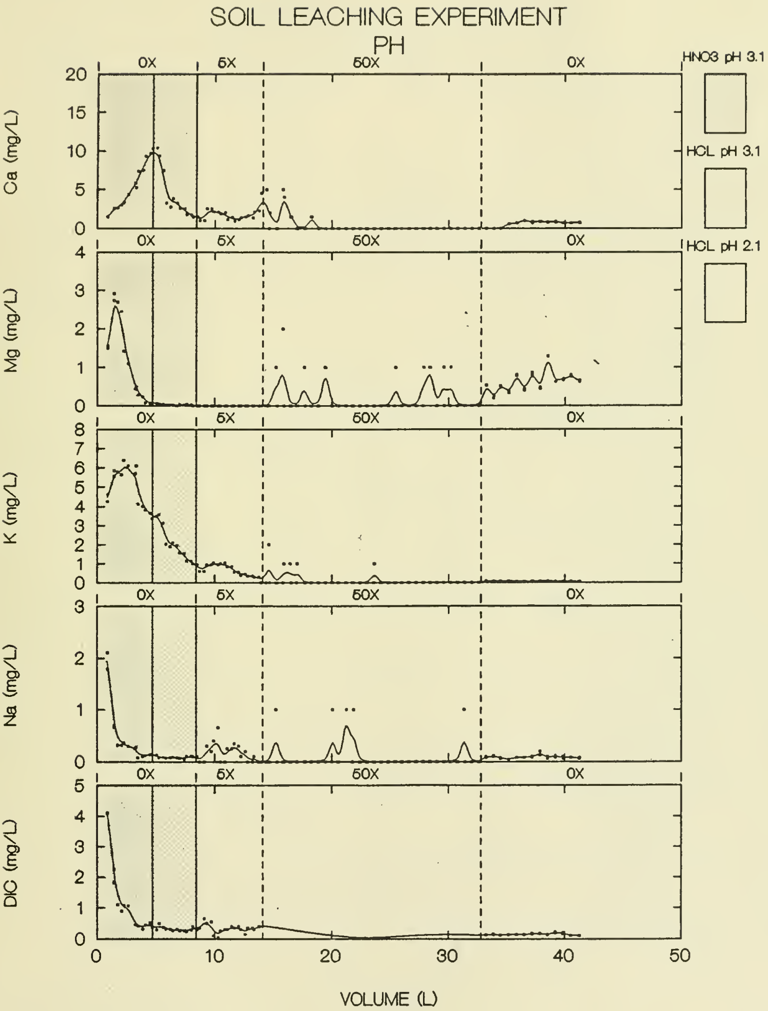

SOIL LEACHING EXPERIMENT
PH
0X
5X
50X
0X
HNO3 pH 3.1
HCL pH 3.1
HCL pH 2.1
Ca (mg/L)
Mg (mg/L)
K (mg/L)
Na (mg/L)
DIC (mg/L)
0
5
10
15
20
0
1
2
3
4
0
1
2
3
4
5
6
7
8
0
1
2
3
0
1
2
3
4
5
0
10
20
30
40
50
VOLUME (L)

Fig. 3c

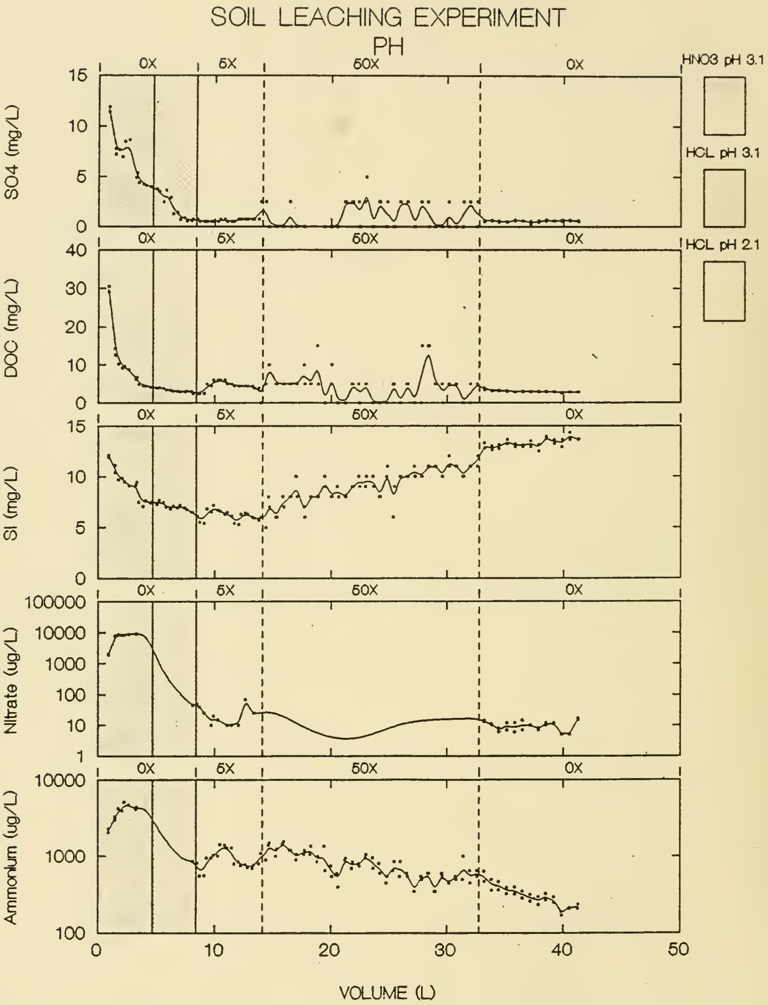

SOIL LEACHING EXPERIMENT
PH
0X
5X
50X
0X
HNO3 pH 3.1
HCL pH 3.1
HCL pH 2.1
SO4 (mg/L)
0
5
10
15
DOC (mg/L)
0
10
20
30
40
SI (mg/L)
0
5
10
15
Nitrate (ug/L)
1
10
100
1000
10000
100000
Ammonium (ug/L)
100
1000
10000
0
10
20
30
40
50
VOLUME (L)

Fig. 4a

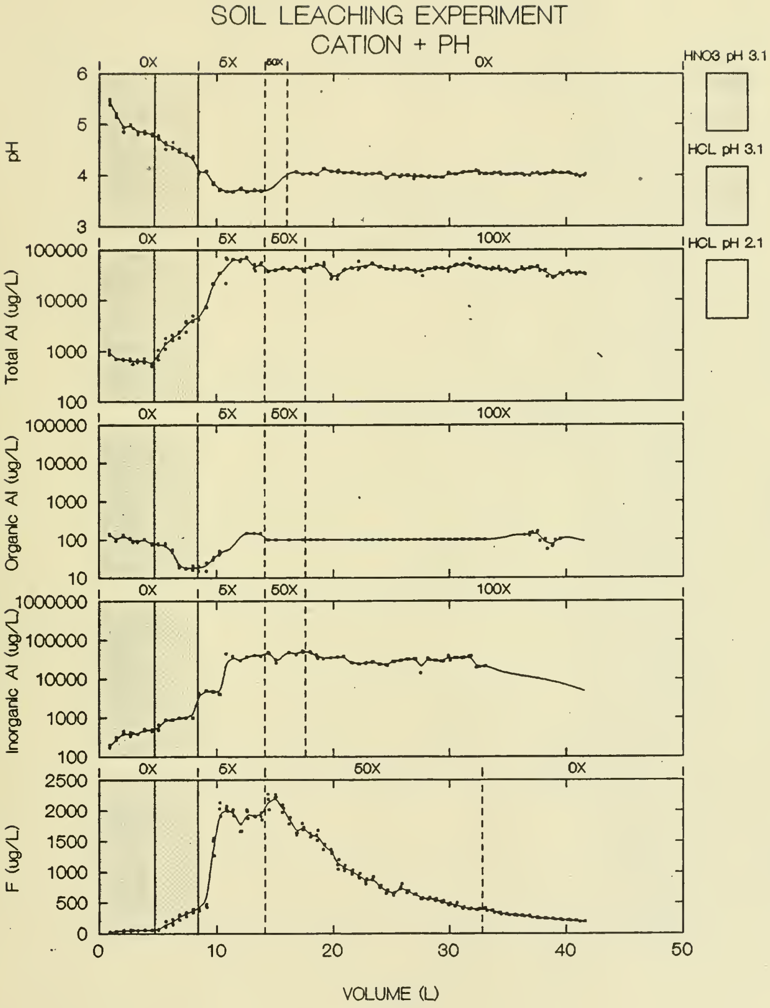

SOIL LEACHING EXPERIMENT
CATION + PH
0X
5X
50X
0X
HNO3 pH 3.1
HCL pH 3.1
HCL pH 2.1
pH
6
5
4
3
0X
5X
50X
100X
Total Al (ug/L)
100000
10000
1000
100
0X
5X
50X
100X
Organic Al (ug/L)
100000
10000
1000
100
10
0X
5X
50X
100X
Inorganic Al (ug/L)
1000000
100000
10000
1000
100
0X
5X
50X
0X
F (ug/L)
2500
2000
1500
1000
500
0
0
10
20
30
40
50
VOLUME (L)

Fig. 4b

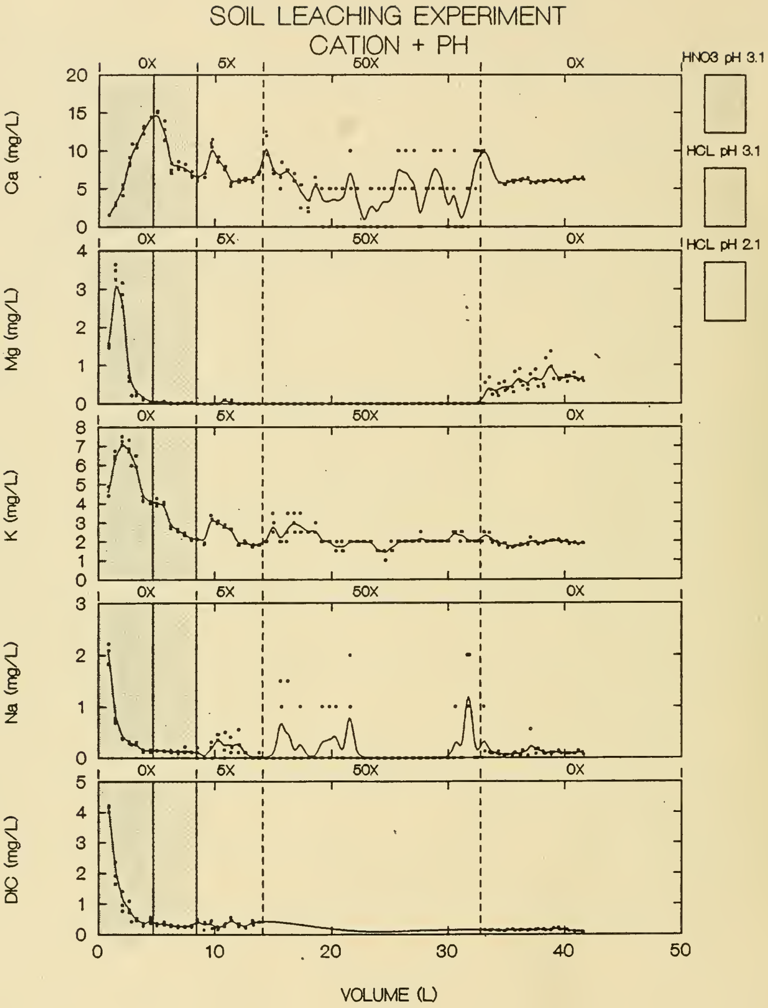

SOIL LEACHING EXPERIMENT
CATION + PH
0X
5X
50X
0X
HNO3 pH 3.1
HCL pH 3.1
HCL pH 2.1
Ca (mg/L)
Mg (mg/L)
K (mg/L)
Na (mg/L)
DIC (mg/L)
0
5
10
15
20
0
1
2
3
4
0
1
2
3
4
5
6
7
8
0
1
2
3
0
1
2
3
4
5
0
10
20
30
40
50
VOLUME (L)

Fig. 4c

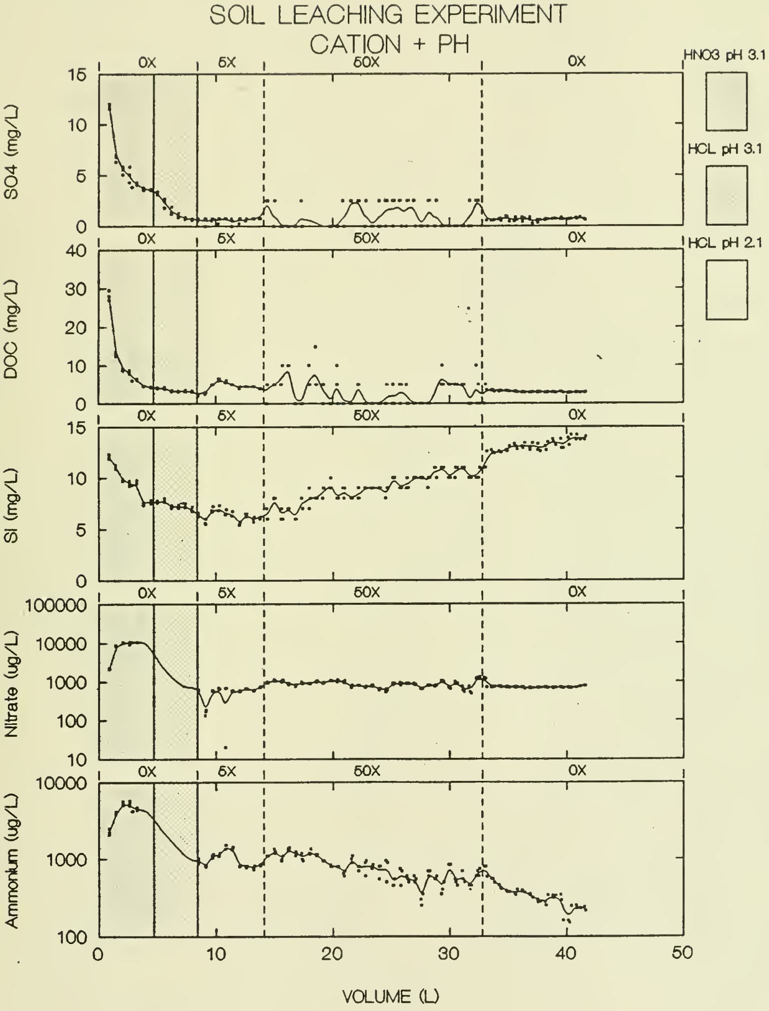
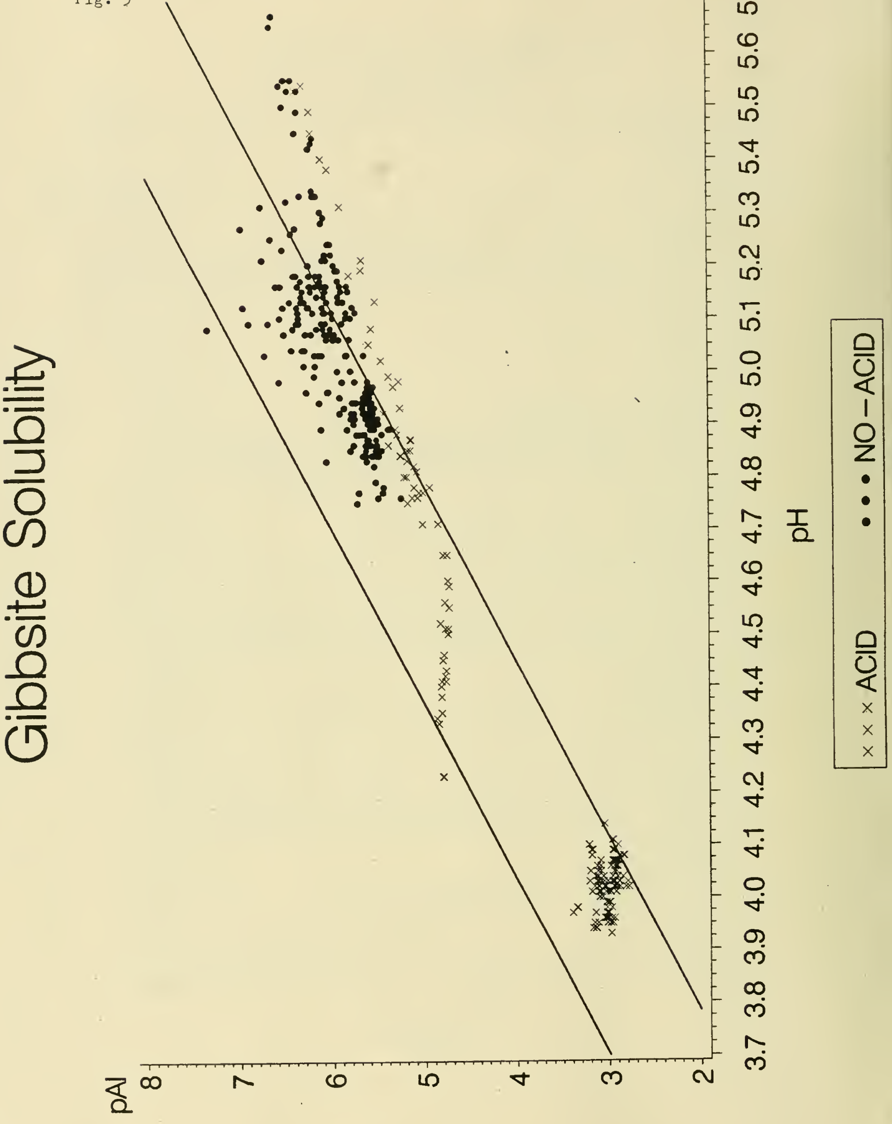

SOIL LEACHING EXPERIMENT
CATION + PH
0X
5X
50X
0X
HNO3 pH 3.1
HCL pH 3.1
HCL pH 2.1
SO4 (mg/L)
0
5
10
15
DOC (mg/L)
0
10
20
30
40
SI (mg/L)
0
5
10
15
Nitrate (ug/L)
10
100
1000
10000
100000
Ammonium (ug/L)
100
1000
10000
0
10
20
30
40
50
VOLUME (L)

Fig. 5


Gibbsite Solubility
pAl
8
7
6
5
4
3
2
pH
3.7
3.8
3.9
4.0
4.1
4.2
4.3
4.4
4.5
4.6
4.7
4.8
4.9
5.0
5.1
5.2
5.3
5.4
5.5
5.6
5.7
× × × ACID
• • • NO-ACID